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Potassium-intercalated H_2Pc films: Alkali-induced electronic and geometrical modifications

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X-ray spectroscopy studies of potassium intercalated metal-free phthalocyanine multilayers adsorbed on Al(110) have been undertaken. Photoelectron spectroscopy measurements show the presence of several charge states of the molecules upon K intercalation, due to a charge transfer from the alkali. In addition, the comparison of valence band photoemission spectra with the density functional theory calculations of the density of states of the H_2Pc^- anion indicates a filling of the formerly lowest unoccupied molecular orbital by charge transfer from the alkali. This is further confirmed by x-ray absorption spectroscopy (XAS) studies, which show a decreased density of unoccupied states. XAS measurements in different experimental geometries reveal that the molecules in the pristine film are standing upright on the surface or are only slightly tilted away from the surface normal but upon K intercalation, the molecular orientation is changed in that the tilt angle of the molecules increases. [http://dx.doi.org/10.1063/1.4738755]

I. INTRODUCTION

Phthalocyanine molecules have been the object of a number of investigations due to their many possible applications in optical and electronic devices.[1,2] The chemical structure of this group of molecules (see Fig. 1), similar to the active sites of chlorophyll, hemoglobin, and different enzymes, makes them appealing as biomimetic catalysts in oxidation reactions.[3,4] Their chemical and thermal stability has permitted studies in ultra high vacuum (UHV) environments resulting in many spectroscopic investigations.[5–18]

The possibility to modify the electronic structure of the molecular film allows the tuning of specific properties and this is clearly highly desired to further improve the performance of Pc-based devices. For this reason, the interesting results reported by Craciun *et al.*[19] and already predicted by a theoretical study by Tosatti *et al.*[20] about the observation of an insulator-to-metal transition of Pc films upon alkali intercalation (between 0 and 4 K atoms per molecule) have inspired a number of studies. A majority of these investigations has dealt with the intercalation of CuPc and other metal Pc (MePc) films by K,[16–19] Rb,[21] and Cs[22,23] with a particular focus on the investigation of the modifications of the electronic structure induced by the alkali. However, a metallic phase has not been observed in any of the mentioned studies.

We here undertake an investigation of K doped H_2Pc and compare the results obtained for this system with the K doped metal Pc's studied in previous works. The lack of a metallic center may largely influence the geometrical arrangement of the K atoms and in turn, alter the electronic structure modification induced by the alkali on the Pc molecules. Photoelectron spectroscopy (PES) was used to map the electronic core and valence levels. In addition, we employed x-ray absorption spectroscopy (XAS), which provides a direct characterization of how the unoccupied molecular orbitals of H_2Pc are affected by K intercalation.

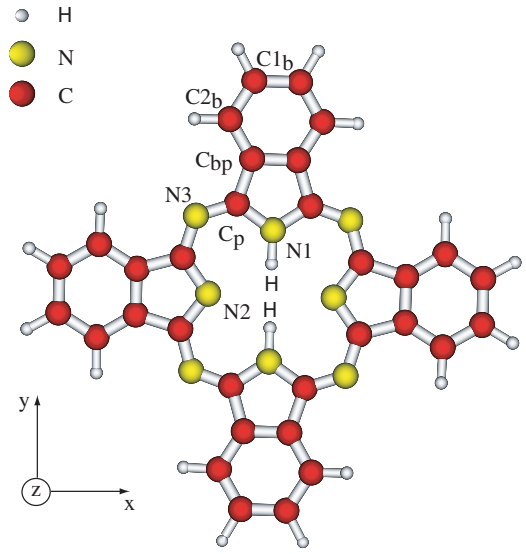

FIG. 1. The structure of metal-free phthalocyanine (H_2Pc), obtained in a single molecule calculation.[6]

II. EXPERIMENTAL

As a substrate, an Al(110) single crystal from the Surface Preparation Laboratory, Zaandam, The Netherlands, was used. The crystal was cleaned by the cycles of Ar^+ sputtering and annealing. H_2Pc was purchased from Aldrich (98% dye content). The molecules were deposited in the preparation chamber under UHV conditions, using a home built evaporator positioned a few centimeters from the substrate surface and carefully outgassed prior to the experiments. The evaporator consisted of a quartz glass tube (with a hole of 3.5 mm diameter) with a tungsten wire winded around for heating. The evaporation rate was controlled by the careful adjustment of the current that heats the glass tube. For all samples examined here, the molecular films were thick enough that no substrate signal could be detected by PES. No contaminants were identified by the PES measurements.

The K intercalation was achieved (in the same preparation chamber) by means of a SAES getter (SAES Getters S.p.A., Lainate (Mi) Italy) source. K was deposited stepwise and the intercalated amount of potassium was determined by measuring the areas of the K2*p* and C1*s* XPS signals, taking into account the PES cross-sections. Both the molecules and the alkali were deposited on the substrate kept at room temperature.

The XAS and PES measurements were performed at beam-line I511,[24] at the MAX-lab synchrotron radiation facility, Lund, Sweden. This undulator based beam-line is equipped with a Zeiss SX700 plane grating monochromator providing high intensity photon flux with energy in the range from 100 to 1500 eV. The beam-line end station houses a Scienta R4000 hemispherical electron energy analyser. The analysis chamber can be rotated around the beam of the incoming linearly polarized light. The construction of the end station results in incoming light always hitting the sample at grazing incidence (7° tilt angle) with respect to the substrate. Therefore, the spectra denoted as "normal emission" are actually 7° off normal. The overall resolution for the C1*s* and N1*s* spectra was 120 meV. For the valence band measurements, the overall resolution was set to 21 meV. All PES spectra shown in this paper were recorded at normal emission and grazing incidence.

For energy scale calibration of the PES data, the C1*s* spectra were measured with first and second order light to know the correct value of the photon energy provided. In addition, a Fermi level position of the clean crystal was used to calibrate the kinetic energy scale of the spectrometer for the chosen values of measurement settings (e.g., slits, pass energy). The binding energy scale of the valence band was also calibrated to the Fermi level of the Al sample by measuring all valence spectra corresponding to different amounts of intercalated potassium in a series during which all adjustable beam-line settings were kept constant. At the end of this series, the Al crystal was sputtered and annealed, and the Fermi level region recorded thereafter.

The x-ray absorption spectra were collected with the Scienta R4000 spectrometer in partial yield mode, i.e., by detecting Auger electrons in a selected kinetic energy window. For the XAS measurements, the photon energy was calibrated by measuring the C1*s* spectra using first and second order light. To correct for time dependent variations in the photon flux and for the monochromator transmission function, the measured XAS signal was divided by the intensity of the incoming light, measured by the photoemission current from a gold grid placed in the path of the light. The monochromator resolutions were 30 meV and 50 meV, for the C1*s* and N1*s* XAS measurements, respectively.

During all measurements, the sample was continuously scanned to avoid beam damage of the molecular film.

III. THEORETICAL METHODS

In this study, we compared the valence band of the H_2Pc film measured by photoelectron spectroscopy with the density of states (DOS) of a single H_2Pc molecule computed by the density functional theory (DFT) calculations using the GAUSSIAN09 program,[25] the same procedure performed for a H_2Pc film in Ref. 11. The geometrical structure of the molecule was fully relaxed imposing a D_{2h} symmetry. The B3LYP exchange-correlation functional[26] and the 6-31g(d,p) basis sets were used for all the atoms.[27] The computed DOS of the molecule was convoluted by a Gaussian curve with a full width at half maximum (FWHM) of 0.5 eV. To simulate the electron injection in the H_2Pc from the alkali intercalation of the film, we compared the DOS of the H_2Pc with the DOS of a H_2Pc^- anion, for which we performed the same type of calculations.

Finally a phthalocyanine with two potassium atoms, one per side (K_2Pc), was geometry optimized with the same procedure used for the H_2Pc. For this molecule, no symmetry constraints were imposed. The resulting structure is provided as supplementary material.[28] The potassium atoms are arranged symmetrically over the center of the molecule, at about 1.8 Å from the molecular plane. A similar arrangement for K_2Pc was proposed by Margadonna *et al.*[29] for a slip-stacked assembly of K_2Pc.

IV. RESULTS AND DISCUSSION

A. Photoelectron spectroscopy

PES was used in this work to investigate the molecular electronic structure modifications induced by exposing a H_2Pc thick film to increasing doses of K. PE measurements in normal and grazing emission (not shown here) were also employed to characterize the K distribution within the molecular film. For the very low doses, the results indicated that K atoms were mainly concentrated at the surface of the film. For higher doses, the K was instead found to be more equally distributed within the film.

The C1*s* and K2*p* spectra for different doses are displayed in Fig. 2. To determine the nominal stoichiometry, the relative areas under the K2*p* and C1*s* peaks were measured taking the relative PE cross sections into account. However, since, as pointed out above, the K atoms were found to be not equally distributed, the nominal stoichiometry cannot be considered as an absolute value but as an average over the probing depth. For the first deposition, the area of the K2*p* peak is too

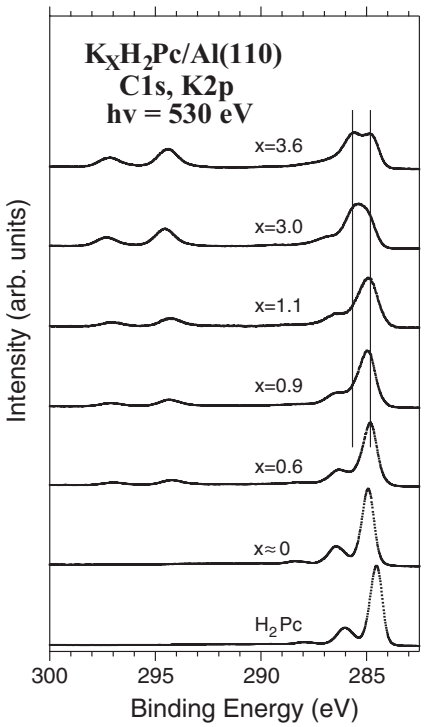

FIG. 2. C1*s* and K2*p* photoemission spectra for pristine H_2Pc and films exposed to different doses of potassium. The spectra have been normalized in intensity so that the area is the same for each spectrum. This allows a clear observation of the change in line-profile for different K doses. With K deposition, the C1*s* line-shape is considerably broadened and at the highest intercalation level, a double structure is seen. Two solid lines mark the peak positions of the features with highest intensity for the intercalation levels x = 0.6 and x = 3.6.

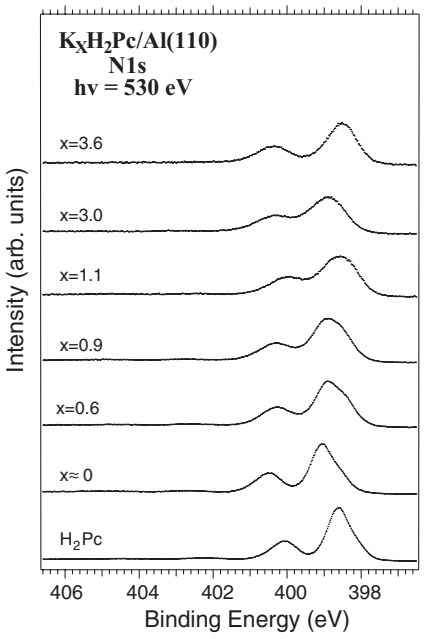

FIG. 3. N1*s* photoemission spectra for pristine H_2Pc and films exposed to different doses of potassium. It is evident that the K intercalation induces several changes to the spectra. A shift towards higher BE and a broadening of the spectra are seen. The spectra have been normalized in intensity so that the area is the same for each spectrum to observe changes in line profile for different K doses.

small to be determined, and these spectra are assigned to the intercalation level x ≈ 0 to indicate that K has been deposited on the film at a very low dose. For the pure H_2Pc film, seen at the bottom of Fig. 2, the C1*s* spectral line consists of three well separated features. The origin of these peaks has been characterized in a previous study by Brena *et al.*,[30] which found that the main feature (at about 284.5 eV) stems from the contribution of the benzene carbons (C_b, see Fig. 1), whereas the peak at about 286 eV is a superposition of features, due to the contribution of pyrrole carbons (C_p, see Fig. 1) and to shake-up processes related to the benzene carbons. The third feature, at about 288 eV, is due to shake-up excitations mainly related to the pyrrole carbons.

After the first K deposition, the C1*s* spectrum is shifted towards higher binding energies (BE) with about 0.4 eV and just slightly broadened. The observed shift of all features is ascribed to a shift of the position of the Fermi level in the density of states, due to the filling of initially empty states upon charge transfer from the alkali. At the intercalation level, x = 0.6, the main C1*s* feature has shifted back by about 0.1 eV and a considerable broadening is observed, implying a clear modification of the molecular electronic structure induced by the interaction with K.

With increasing K dose, the line-shape is further broadened and for the main feature, a small shift in BE towards higher values is noted with respect to the position observed for x = 0.6. It can also be noted that for intercalation levels above x = 0.9, no shake-up signal is observed. At x = 3.0, the whole spectrum is shifted to higher binding energy (this is observed also for the N1*s* photoemission line shown in Fig. 3) and moreover, it is obvious that a component at high binding energy gives a major contribution to the spectrum. For x = 3.6, this latter feature becomes dominating. Also, it can be noted that the K2*p* doublet at 294.1 eV and 297.1 eV is seen to shift slightly with K intercalation and the energy shift is comparable to that observed for the valence features, as will be shown later.

The N1*s* photoemission spectra collected for different K doses are shown in Fig. 3. The curve at the bottom displays the spectrum of H_2Pc, which consists of an asymmetric main feature at about 398.6 eV, due to ionization of the N2 and N3 atoms (see Fig. 1), and a feature at higher BE (at about 400 eV), due to ionization of the N1 atoms.[6]

After the first K deposition, the whole spectrum is seen to shift by about 0.4 eV towards higher BE and to slightly broaden. For the next intercalation step (x = 0.6), the main feature of the N1*s* spectrum is shifted back with about 0.15 eV (towards lower BE), and the line-shape is considerably modified, showing a pronounced asymmetry of the main feature. At x = 0.9, a slightly broader spectrum has been recorded and at x = 1.1, it further shifts towards lower BE values. For the high intercalation levels (x = 3.0), the line-shape is even more smeared out and shifted to higher BE values compared to the x = 1.1 case. At x = 3.6, the overall spectrum is significantly changed, with a remarkably larger energy separation between the main feature and the peak at high BE.

The observed changes in line profile and width of the C1*s* and N1*s* spectral lines are similar to those observed for other MePc's and attributed to a lowering of the molecular symmetry caused by the adsorption of the alkali in specific sites with

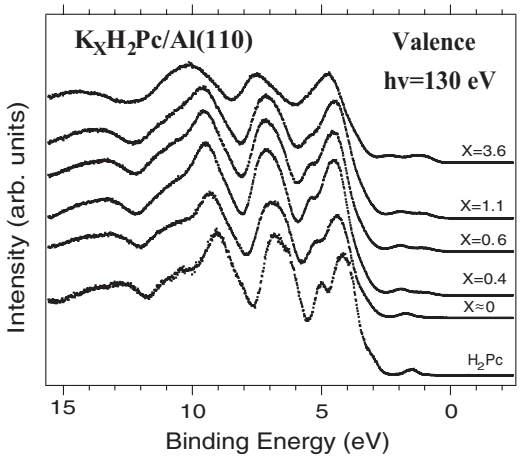

FIG. 4. Valence band photoemission spectra for pristine H_2Pc and films exposed to different doses of potassium. The intensity of the spectra has been normalized at 25 eV BE.

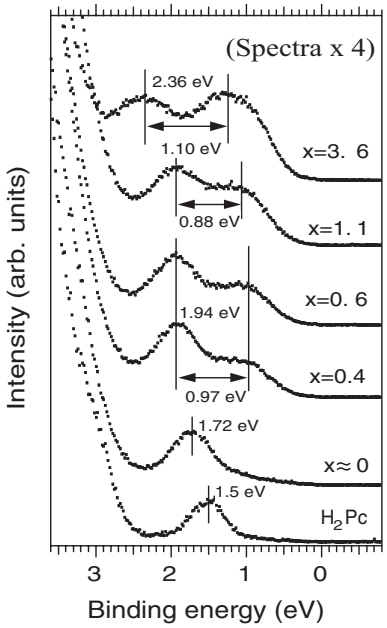

FIG. 5. Valence band photoemission spectra ($h\nu = 130$ eV) showing the HOMO and LUMO-derived features for pristine H_2Pc and films exposed to different doses of potassium (top spectra highest K concentration).

respect to the molecule. Previous studies have proposed some adsorption site for the alkali like, for example, for K on FePc[31] and on CuPc[16] films and others have proposed that K atoms would form two different stoichiometric phases, namely K_2Pc and K_4Pc depending on the alkali intercalation.[18] However, for other MePc's like MnPc, some investigations have proposed the possible formation of a KMePc phase in addition to the two already mentioned phases.

In light of these results, we can compare our results and summarize that, in contrast to the findings for potassium intercalation of FePc by Aristov *et al.*,[31] in our study for increasing K doses, we cannot see any significant shift in BE position of the peak centered at 286.3 eV and attributed to pyrrole-like C in the pristine H_2Pc film. Furthermore, we cannot neglect a remarkable broadening of the peak related to the benzene-like carbon atoms. However, as observed by Aristov *et al.*,[31] we see a broadening of the N1*s* line for the different potassium doses, indicating that the pyrrole atoms are probably the most affected by alkali adsorption. A more detailed discussion of our results with respect to the adsorption site for the potassium atoms will be the focus of a future paper.

Valence band (VB) spectra for different x are shown in Fig. 4. The spectral features shift in binding energy to higher values and a broadening of all states is observed after the addition of K to the molecular film. For each alkali deposition, the intensity of the K3*p* peak at about 18.6 eV increases (not shown).

The spectral region close to the Fermi level is displayed in Fig. 5. Already after the first K deposition, a shift of about 0.2 eV is seen towards higher BE of the highest occupied molecular orbital (HOMO). This feature further shifts for the next depositions, but stays fixed at 1.94 eV for the intercalation levels x between 0.4 and 1.1 eV. For even higher K doses, a further shift of about 0.4 eV is observed.

Further modifications are observed in the valence spectra for different K doses (Fig. 5). The spectrum of the pristine film presents a HOMO at about 1.5 eV. The VB of the doped film is characterized instead by a splitting of the HOMO peak into two sub-peaks, at approximately 0.9 and 1.9 eV.

All these features, the single peak for the pristine film and the two peaks for the doped film, are well reproduced in the DOS of the theoretical simulations shown in Fig. 6 (peak A for the pristine HOMO and A_1 A_2 for the two sub-peaks). The measured PE spectrum for the undoped H_2Pc and for the $K_{1.1}H_2Pc$ films are compared to the DOS of the single H_2Pc molecule and of a H_2Pc^- anion. The theoretical spectra are shifted in energy in order to be aligned to the top of peak B in Figure 6, which lies at about 4.40 eV for $K_{1.1}H_2Pc$ and at about 4.04 eV in the pristine film. The DOS of the H_2Pc was shifted by 3.0 eV. The DOS of the anion was shifted by 0.45 eV.

The orbital pictures obtained from B3LYP/DFT calculations of the HOMO and LUMO of the H_2Pc and of the HOMO, HOMO-1, and HOMO-2 of the anion (H_2Pc^-) are presented in the right panel of Fig. 6. The computed electronic states of the H_2Pc are doubly degenerate; the HOMO has a_u symmetry and the LUMO b_{2g} symmetry. The H_2Pc^- anion can be considered as an analogy for the electron injection from the alkali to the molecule. The extra electron in the anion lifts the spin degeneracy of the electronic states and occupies the empty b_{2g} LUMO orbital of neutral H_2Pc. As seen in Fig. 6, the HOMO of the anion is very similar to the H_2Pc LUMO, confirming that the new peak at the lowest BE in the valence band photoemission of the intercalated films is due to the occupancy of the molecular LUMO (now anion HOMO) by the alkali electron transfer. This charge transfer translates into a shift of the Fermi level and explains the binding energy shift of the features observed in C1*s* and N1*s* PE spectra as already proposed for MePc's in previous studies.[18,31] A different electronic structure characterizes the K_2Pc, where the degenerate HOMO has the same symmetry and composition as those of the H_2Pc.

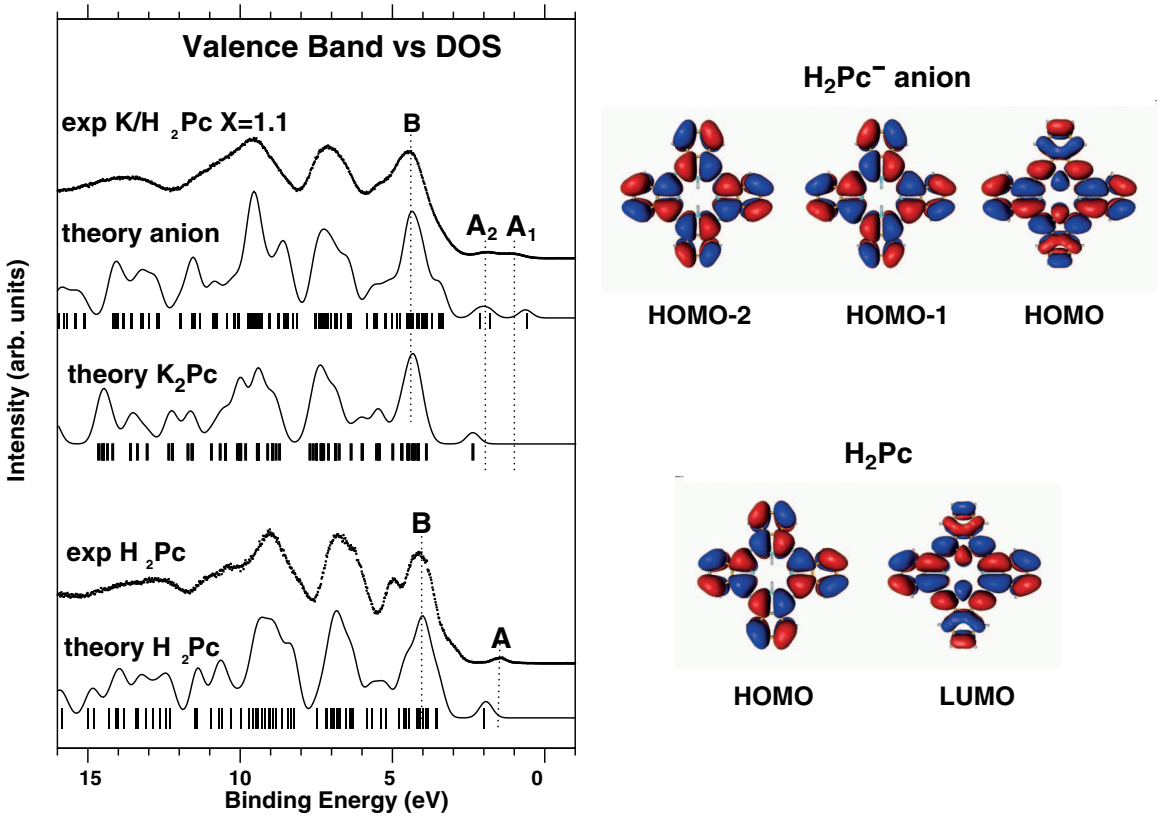

FIG. 6. (Left panel) Comparison of experimental valence band photoemission spectra for pristine and K-intercalated H_2Pc films. Solid lines represent the theoretical simulations of the spectra considering a single H_2Pc molecule, an anion (H_2Pc^-), and a K_2Pc. (Right panel, bottom) DFT picture of HOMO and LUMO orbitals of single H_2Pc molecule; (upper part) HOMO-2, HOMO-1, and HOMO of H_2Pc^- anion. The images show the similarity between the HOMO of the anion and the LUMO of the pristine H_2Pc.

We have further considered the possibility of dehydrogenation of the H_2Pc in its central part with a loss of the two central hydrogens, and the formation of a potassium phthalocyanine. In Fig. 6 we have modeled a K_2Pc molecule, which would simulate the K-Pc stacking proposed in Ref. 29, considering one K per each side of the molecule. However, in our present K-doping experiment, we have not followed any procedure similar to mentioned study where K-Pc was synthesized starting from CuPc molecules in gas phase. Our calculation of the K_2Pc DOS shows a single HOMO feature, in contrast with our spectroscopic measurements of the doped film. Moreover, the central hydrogens, seem to be present in at least a large part of the molecules throughout the K intercalation, since in the N 1s PES measurements, the peak at about 400 eV, which is the characteristic signature of the N atoms bonded to H, can clearly be seen at every doping level.

Even though we cannot exclude the formation of some KPc or K_2Pc, we have anyway strong evidence that such a synthesis is not a main process occurring during the doping.

For none of the intercalation levels, we detected any spectral intensity at the Fermi level, in other words: no metallic phase is ever observed.

B. X-ray absorption spectroscopy

In a XAS measurement, the incoming light resonantly excites an electron from a core level to an initially empty valence level. This technique therefore allows an element specific mapping of the unoccupied levels of a system, although modified by the presence of the core hole. The XAS process is governed by the dipole selection rule and by using polarized synchrotron radiation, the symmetry of different orbitals can be probed.[26] The spectral intensity of specific features depends on the orientation of the molecular plane with respect to the E-vector of the incoming light. By examining the angular dependence of the intensity of the absorption features one can therefore determine the geometrical orientation of the molecules with respect to the surface.

In this work, we present both C1*s* and N1*s* XAS data. In Fig. 7, the long range N1*s* XAS spectra measured for different intercalation levels, from x = 0 to x = 3.0 are displayed. To the left are spectra recorded with the E-vector of the light parallel to the surface; to the right instead, there are spectra for the same stoichiometries but measured with the E-vector perpendicular to the surface.

In the spectra of the pristine H_2Pc film, there are clear differences between the two geometries: for the E-vector parallel to the surface, the features in the region 398–400 eV have the highest intensity, while for the other geometry, the dominant spectral intensity is found for $h\nu > 405$ eV.

From a previous XAS study[6] of H_2Pc, it is known that the spectra weight around 399 eV is due to excitations into initially unoccupied π_z orbitals, directed out of the molecular plane, while the intensity between 403 and 425 eV stems from excitations into σ-type orbitals, with contributions mainly from states in the molecular plane. The intensity relationship

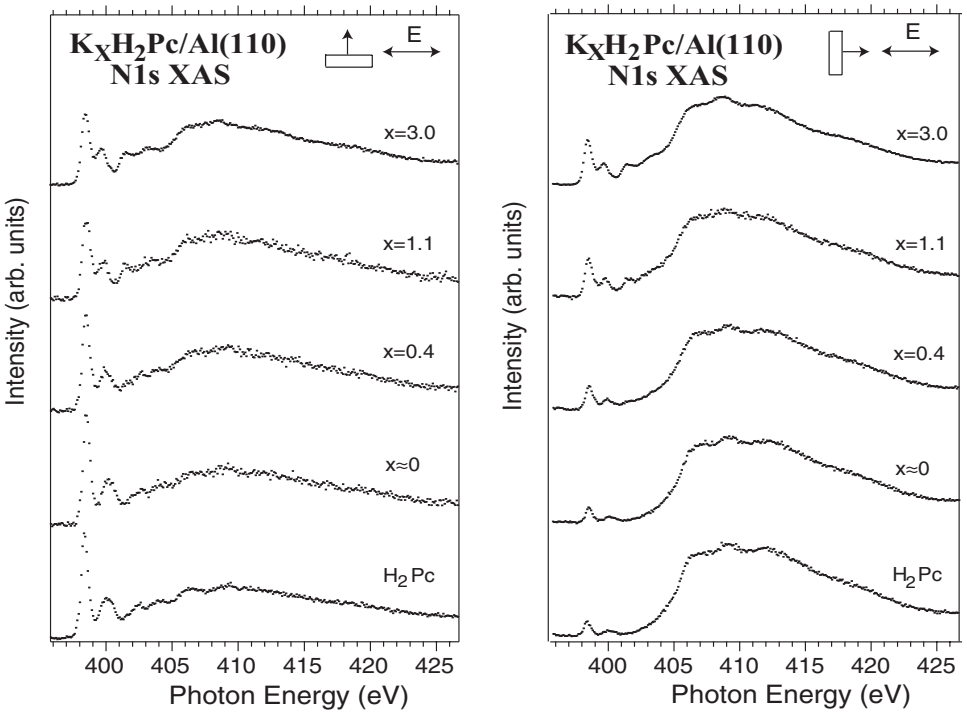

FIG. 7. N1*s* x-ray absorption spectra measured for pristine H_2Pc and for different potassium intercalated films, in two geometries (as indicated schematically in the upper right corner of each spectral series). The data in the left panel were recorded with the E-vector parallel to surface, those in the right panel were instead measured in the geometry with the E-vector of the light perpendicular to the surface. Comparing the former, one notices that the intensity of the π^* features (around 398–402 eV) decreases with increasing K content. Comparing the latter, one sees instead that with higher K content the intensity of the π^* features increases relative to the intensity of the σ features.

between the π^* and σ^* features are different in the two measurement geometries. The fact that the excitations into orbitals directed out of the molecular plane are predominant in the geometry where the E-vector is parallel to the surface and, in the other experimental geometry, the features related to excitations into orbitals in the molecular plane are most intense, clearly indicates that the molecules within the H_2Pc film are standing upright with respect to the surface plane (or at least are highly tilted towards the surface normal).

For the changes induced by potassium intercalation into the organic matrix, let us focus on the XAS spectra measured with the E-vector parallel to the sample surface (left hand side in Fig. 7). After the first K deposition, the overall spectral structure is unchanged but all spectral features are shifted by about 0.1 eV towards higher photon energy. Upon further K deposition, several considerable changes are observed, as can be seen in Fig. 7 and in more detail in Fig. 8, which shows a close-up on the region between 397–402 eV for the two experimental geometries. First, the asymmetry at 397.8 eV of the main spectral feature (evidenced by the arrows in the figure) is quenched when x exceeds 0.4 in K_xH_2Pc films; second, the energy separation between the two π^* features between 398 and 401 eV decreases with increasing K content and, in the geometry with the E-vector perpendicular to the surface, the intensity of the features between 398 and 403 eV are increased relative to that at $h\nu = 410$ eV. Third, also features at higher energies are seen to be affected and shifted in energy towards lower photon energy. Fourth, the intensity of the main feature, related to excitations into the unoccupied orbitals of π-symmetry, decreases for higher K doses.

The C1*s* XA spectra recorded in the two experimental geometries for pristine H_2Pc and for different potassium intercalated films are shown in Fig. 9. As in the case of N1*s* XAS, after the first potassium dose, a small shift of the whole spectrum is observed when studying the spectra taken with the E-vector parallel to the surface, but here this goes hand in hand with a considerable intensity decrease of the π^* feature at about 285.5 eV; this effect is even more pronounced for the case of $K_{0.4}H_2Pc$.

The spectra taken with the E-vector of the light perpendicular to the surface (Fig. 9) show the same trend observed in the N1*s* XA spectra, namely an intensity increase of the π^* symmetry feature at $h\nu = 285.5$ eV with increasing K dose. In both geometries, two features due to excitations from the K2*p* level are observed at about 297 and 300 eV for K_xH_2Pc films with $x \geq 0.4$.

In Fig. 10, the spectral region between 283 and 292 eV is displayed, showing dramatic changes with K intercalation. In the case where the E-vector of the light is parallel to the surface, the intensity of the π^* peak observed at lowest photon energy for the H_2Pc film is significantly decreased already for $K_{0,4}H_2Pc$; in addition, a fine structure of the main peak at 284.7 eV, observed for the H_2Pc and at the lowest K doses can no longer be distinguished for higher K doses. For $x = 1.1$ and $x = 3.0$, the structure of the main feature is strongly altered, and the features at energies between 287 and 291 eV are shifted in photon energy.

To sum up, upon the intercalation of potassium into the H_2Pc film, important changes in the intensity of the π^* resonances were observed in both N1*s* (Fig. 6) and more

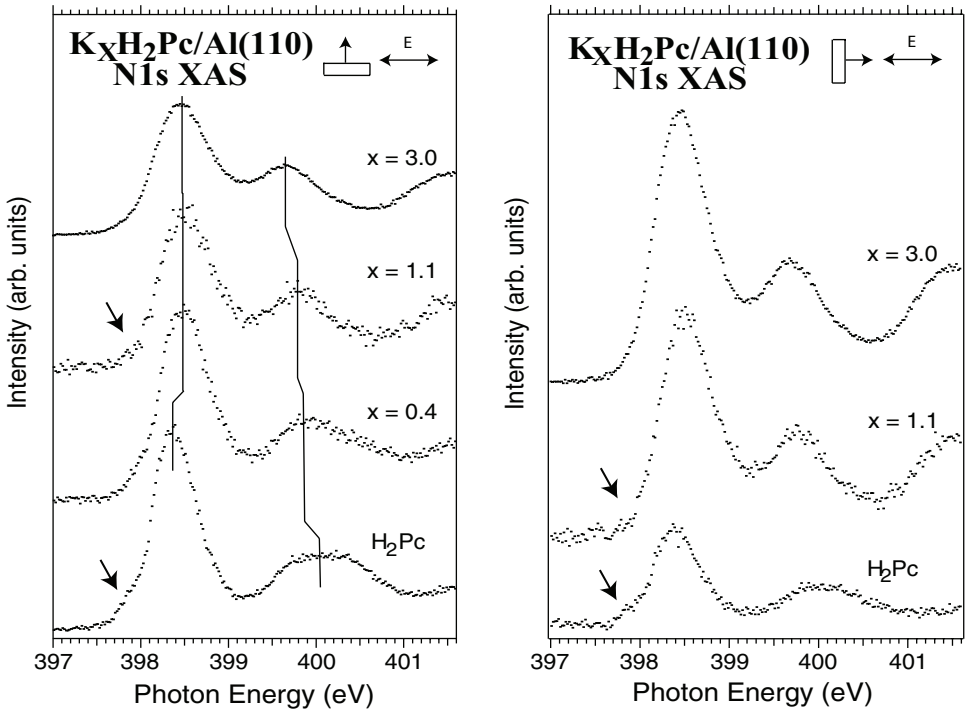

FIG. 8. Detailed N1*s* x-ray absorption spectra for pristine H_2Pc and for different potassium intercalated films. The spectra in the left panel were recorded with the E-vector parallel to surface, the ones in the right panel with the E-vector perpendicular to surface. The arrows indicate the changes of the threshold intensity for increasing K dosing.

evidently in C1*s* XAS spectra (Fig. 8) for the two experimental geometries. Of course, the intensity variation observed for the threshold features can be related to the alkali charge donation that changes the occupancy of the molecular orbital. The intensity decrease and the changes of the spectral features are more pronounced in the C1*s* than in the N1*s* XA spectra due to the larger contribution from the C atoms to molecular LUMO. This is confirmed by our calculation, which indicates that the

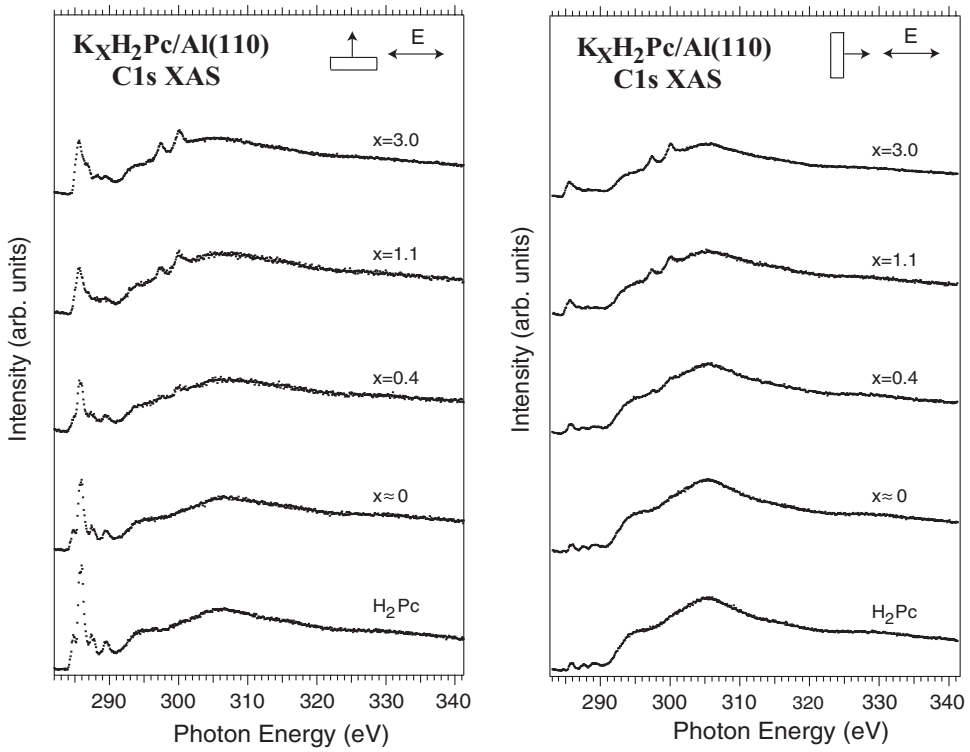

FIG. 9. C1*s* x-ray absorption spectra measured for pristine H_2Pc and for different potassium intercalated films. The spectra in the left panel were measured with the E-vector parallel to the surface and the ones in the right panel with the E-vector perpendicular to the surface geometries. The two features at about 297 and 300 eV are due to excitations from the K2*p* level.

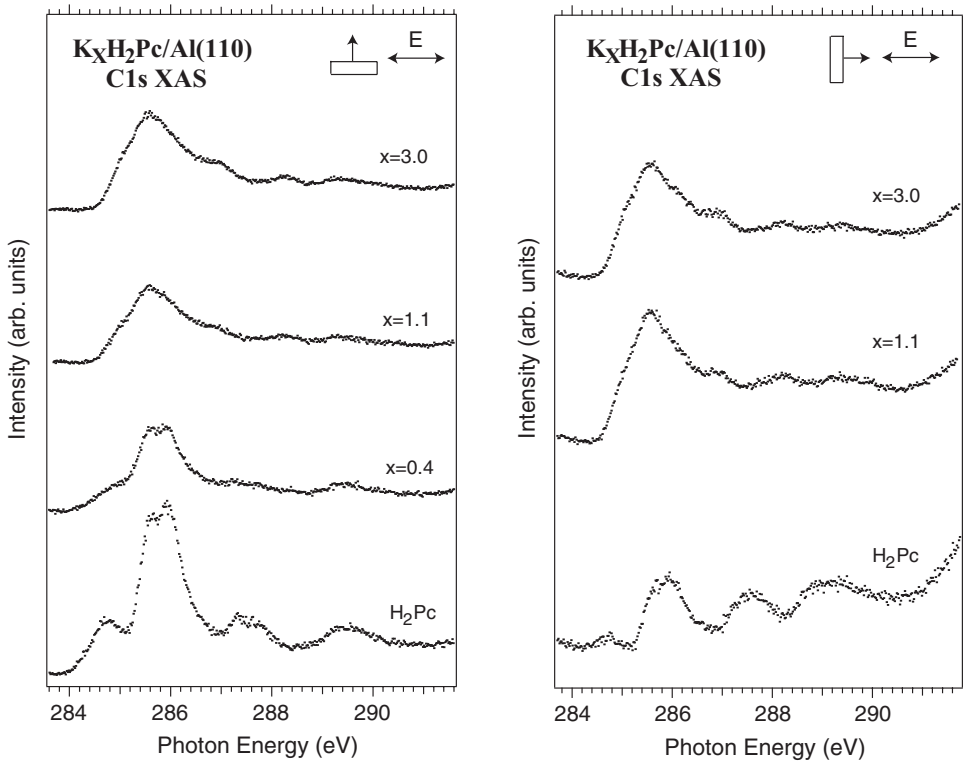

FIG. 10. C1*s* x-ray absorption spectra in the region 283.5 to 291.6 eV for pristine H_2Pc and for different potassium intercalated films. The spectra in the left panel were recorded with the E-vector of the light parallel to the surface, and the ones in the right panel with the E-vector perpendicular to the surface.

molecular LUMO is composed of 74% C2*p* and 24% N2*p* orbitals. Moreover, in the detailed N1*s* XAS spectra in Fig. 7, a shift of the features at 400 eV to lower photon energies for increasing K doses is clearly evident. This shift can be related not only to the chemical shift seen in the photoemission spectra, but also to the increased occupancy of antibonding molecular orbital.[31,32] However, in Fig. 6, it is possible to observe that the π^* resonance intensity decreases in the spectra taken in one experimental geometry (E parallel to the surface), but increases in the other (E perpendicular to the surface). Figure 11 shows the relative intensity changes of the π^* and σ^* resonances for the pristine H_2Pc film and for the film with stoichiometry K_3H_2Pc. These results indicate that the molecules change their orientation upon potassium intercalation. Very interestingly, in previous works,[31,33] a α to β phase transition has already been predicted for the Pc molecular films intercalated with alkalis. The broadening of the photoemission lines could therefore be attributed to this molecular re-orientation and/or increased disorder.

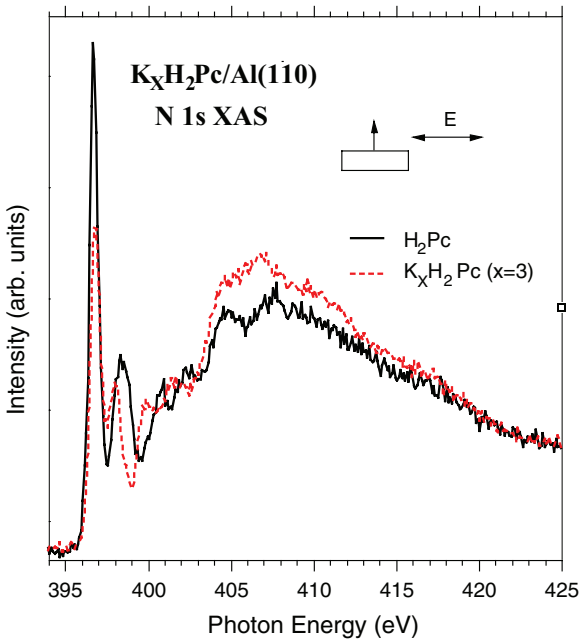

FIG. 11. N1*s* x-ray absorption spectra of a pristine H_2Pc (black solid line) and a potassium-intercalated film, with stoichiometry K_3H_2Pc (red dotted line), taken with the E-vector of the light parallel to the surface. The data show the reorientation of the molecules upon potassium intercalation.

V. CONCLUSIONS

Potassium intercalation of H_2Pc multilayers was studied by spectroscopic techniques (PES and XAS) and theoretical DFT simulations. For different intercalation levels, the C1*s*, K2*p*, N1*s*, and valence spectra were recorded and the N1*s* and C1*s* x-ray absorption spectra were collected in two different geometrical orientations.

The XPS results reveal binding energy shifts of all features, attributed to a shift of the Fermi level of the system due to the filling of previously empty molecular states. The presence of several charge states of the molecules in the film, induced by different charge donation from the alkali, results in a broadening of the C1*s*, N1*s*, and valence levels upon K intercalation. In the region close to the Fermi level, the filling of the formerly empty LUMO by the charge from the alkali

is observed as the appearance of a new spectral feature. This is confirmed by the very good agreement between the experimental data and the theoretical simulation of the valence data for an anion H_2Pc^-. It is therefore evident that the intercalation results in a charge transfer from the K to the H_2Pc, also confirmed from the measured XAS data, showing an intensity change of the LUMO related features.

Furthermore, the N1*s* XA measurements reveal that the tilt angle of the molecular plane relative to the surface is increased at higher K intercalation levels, i.e., a re-orientation of the molecules upon K intercalation takes place. In addition, the line-shape is changed for several features and shifts in photon energy are also observed testifying the molecular electronic structure modification induced by the interaction with the alkali.

No intensity at the Fermi level could be detected at any K dose, demonstrating that there is no metallic phase of the system.

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